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Title of the invention Pigment dispersant and pigment composition

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Specification

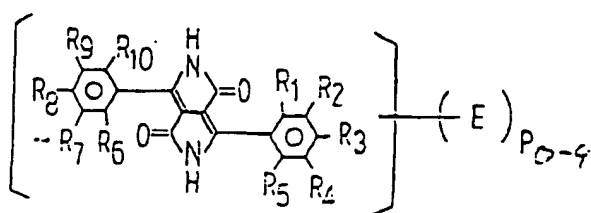
1. Title of the invention.

5 Pigment dispersant and pigment composition

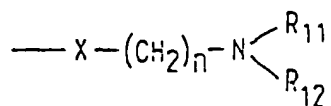
2. Scope of the patent claims

1. A pigment dispersant represented by formula (I)

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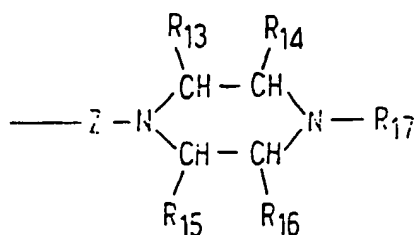


(where E represents



15

or



20

R₁ to R₁₀ each independently represent a hydrogen atom or halogen atom or alkyl, alkoxy, cyano, sulfonyl, carboxyl, dialkylamino, haloalkyl, alkoxy carbonyl, alkylmercapto, carbamoyl or sulfamoyl group;

25 P represents 0 or an integer not greater than 4;

X represents a direct bond or -SO₂NH-, -CONH-, -CH₂NHCOCH₂NH- or -(CH₂)_mNH- (where m represents an integer from 1 to 10);

R_{11} and R_{12} independently represent an optionally substituted saturated or unsaturated alkyl group, or R_{11} and R_{12} represent an optionally substituted heterocyclic ring containing a sulfur, oxygen or nitrogen atom;

5 n represents an integer from 1 to 20, but is an integer from 1 to 10 when X is a direct bond;

Z represents $-SO_2-$, $-CO-$, $-CH_2NHCOCH_2-$, $-SO_2NH-$, $-CONH-$, $-CH_2NHCOCH_2NH-$ or $-(CH_2)_mNH-$ (where m represents an integer from 1 to 10);

10 R_{13} , R_{14} , R_{15} and R_{16} each independently represent a hydrogen atom or an optionally substituted saturated or unsaturated alkyl group or aryl group; and

R_{17} represents an optionally substituted saturated or unsaturated alkyl or aryl group.

15

2. A pigment composition comprising pigment and pigment dispersant according to claim 1.

3. Detailed description of the invention

20

[Aim of the invention]

[Fields of industrial use]

The present invention relates to a pigment dispersant
25 for the provision of a pigment dispersion having excellent suitability for use, specifically, excellent non-aggregating properties, amorphous properties and fluidity.

30 [Prior art]

Generally, finely particulate pigments are used in practice for achieving distinct color tone and high coloring strength in various ink compositions and
35 coatings. However, the fine pigment particles are known to cause various problems in that it is difficult to achieve a stable dispersion when they are dispersed in offset inks, gravure inks, coatings and other such non-aqueous vehicles, and this has a considerable effect on

the production operations and on the value of the resulting products.

For example, not only are dispersions which contain fine particulate pigments occasionally highly
5 viscous, rendering removal from the dispersing apparatus and transportation difficult, but, in the worst cases, they form gels during storage, which renders them difficult to use. Moreover, mixing different pigments can result in color separation due
10 to flocculation, and a marked deterioration in coloring strength and uneven coloration in vehicle products, due to a decrease in sedimentation and the like. The coating film surface of the vehicle product is also poor, exhibiting decreased luster, poor leveling and
15 the like.

Although this does not directly affect the pigment dispersion, in some organic pigments there are phenomena which accompany changes in the crystal properties of the pigment.

20 Specifically, conferring stability by changing the shape and size of crystalline particles of pigments that are energetically unstable in non-aqueous vehicles such as gravure ink and offset ink results in marked changes in hue, a deterioration of coloring strength
25 and the occurrence of coarse particles and the like, which adversely affect the commercial value of the vehicle product.

There have been many suggestions to date for overcoming the various problems described above, and
30 these suggestions center on copper phthalocyanine and quinacridone-based pigments.

These suggestions can be classified, according to the technological methods involved, into the following two broad types of method.

35 The first method, as seen in USP 3370971 and USP 2965511, involves covering the surface of pigment particles using a colorless compound such as tertiary butylbenzoic acid, aluminum oxide or silicon oxide.

The second method, as typified in Japanese Examined Patent Publication Number S41-2466 and USP 2855403, involves admixing a compound obtained by introducing substituent group(s) such as sulfone, sulfonamide, aminomethyl and/or phthalimidomethyl group(s) onto side chains of an organic pigment matrix.

Compared to the first method, the second method is much more advantageous in terms of the non-aggregating properties and crystalline stability of the pigment in non-aqueous vehicles, and it is also a very useful method when judged in terms of ease of pigment composition production.

[Problems to be overcome by the invention]

The present invention provides a dispersion method and pigment composition with which it is possible to obtain a stable dispersion of excellent fluidity and non-aggregating properties when offset ink, gravure ink, coatings and the like are produced.

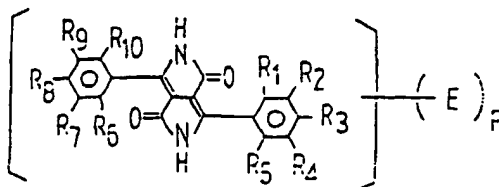
[Constitution of the invention]

[Means of overcoming the problems]

The present invention relates to pigment dispersant represented by formula (I), and pigment composition comprising pigment and pigment dispersant represented by formula (2).

Formula (I)

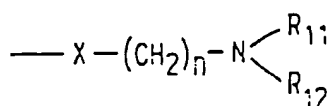
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(where E is as defined above)

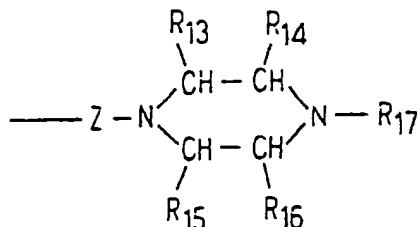
In formula (I), R_1 to R_{12} each independently represent a hydrogen atom or halogen atom or alkyl, alkoxy, cyano, sulfonyl, carboxyl, dialkylamino, halo-alkyl, alkoxycarbonyl, carbamoyl, alkylmercapto or
 5 sulfamoyl group, and hydrogen, chlorine, bromine, cyano, methyl, ethyl, trifluoromethyl, dimethylamino, diethylamino, sulfonyl, carboxyl, methoxy, ethoxy, *tert*-butyl and methoxycarbonyl groups are preferred.

Moreover, in formula (I), the amino components
 10 used to form formula



or formula

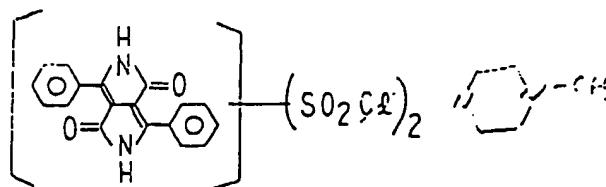
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include, for example, dimethylamine, diethylamine, N-ethylisopropylamine, N-ethylpropylamine, N-methyl-
 20 butylamine, N-methylisobutylamine, N-butylethylamine, N-*tert*-butylethylamine, diisopropylamine, dipropylamine, N-*sec*-butylpropylamine, dibutylamine, di-*sec*-butylamine, diisobutylamine, N-isobutyl-*sec*-butylamine, diamylamine, diisoamylamine, dihexylamine,
 25 di(2-ethylhexyl)amine, dioctylamine, N-methyloctadecylamine, dodecylamine, diallylamine, N-ethyl-1,2-dimethylpropylamine, N-methylhexylamine, 2-hydroxymethylaminoethanol, diallylamine, distearylamine, N,N-dimethylaminomethylamine, N,N-dimethylaminomethylamine,
 30 N,N-dimethylaminopropylamine, N,N-dimethylaminoamylamine, N,N-dimethylaminobutylamine, N,N-diethylaminoethylamine, N,N-diethylaminopropylamine,

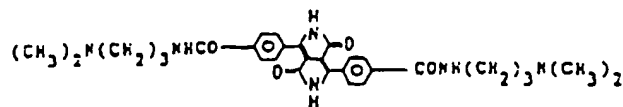
- N,N-diethylaminohexylamine, N,N-diethylaminobutylamine,
 N,N-diethylaminopentylamine, N,N-dipropyl-
 aminobutylamine, N,N-dibutylaminopropylamine, N,N-
 dibutylaminoethylamine, N,N-dibutylaminobutylamine,
 5 N,N-diisobutylaminopentylamine, N,N-methyl-
 laurylaminopropylamine, N,N-ethylhexylaminoethylamine,
 N,N-distearylaminooethylamine, N,N-diolel-
 aminoethylamine, N,N-distearylaminobutylamine, piperi-
 dine, 2-pipecoline, 3-pipecoline, 4-pipecoline, 2,4-
 10 rubetidin, 2,6-rubetidin, 3,5-rubetidin, 3-piperidine-
 methanol, pipecolic acid, isonipecotic acid, methyl
 isonipecotate, ethyl isonipecotate, 2-piperidine-
 ethanol, pyrrolidine, 3-hydroxypyrrolidine,
 N-aminoethylpiperidine, N-aminoethyl-4-pipecoline,
 15 N-aminoethylmorpholine, N-aminopropylpiperidine,
 N-aminopropyl-2-pipecoline, N-aminopropyl-4-pipecoline,
 N-aminopropylmorpholine, N-methylpiperazine,
 N-butylpiperazine, N-methylhomopiperazine,
 1-cyclopentylpiperazine and 1-amino-4-methylpiperazine.
 20 There are several synthesis routes for the production
 of pigment dispersant of the present invention, and a
 summary of typical production methods (1) and (2) for
 pigment dispersants represented by formula (II) and
 formula (III) are shown below.

25 Formula (II)



Formula (III)

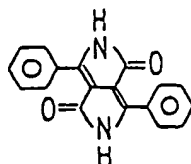
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1) First, compound represented by formula (IV) is prepared by reacting benzonitrile and dimethyl succinate.

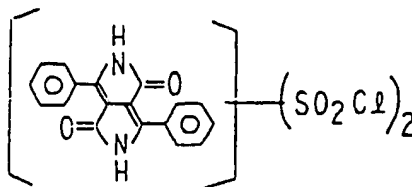
(Formula IV)

5



Next, compound represented by formula (V) is prepared by chlorosulfonating compound represented by formula (IV) by a common method.

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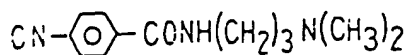
Pigment dispersant represented by formula (II) is then prepared by reacting compound represented by formula (V) with N-methylpiperazine.

15

2) First, compound represented by formula (VI) is prepared by reacting p-cyanobenzoyl chloride with N,N-dimethylaminopropylamine.

20

Formula (VI)



25

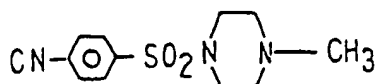
Next, pigment dispersant represented by formula (III) is prepared by reacting compound represented by formula (VI) with dimethyl succinate.

It should be noted that pigment dispersant represented by formula (II) can also be prepared by, for example, first preparing compound represented by

30

formula (VII), then applying the same methods as those used in the production of pigment dispersant represented by formula (III) described in 2) above, although synthesis according to the method described in 5 1) above is more useful industrially.

Formula (VII)



10

Pigment dispersant obtained according to the present invention usually yields excellent dispersions with almost all commercially available pigments. For example, it can be used with azo-type pigments such as condensed azo pigments, soluble and insoluble azo pigments and diketopyrrolopyrrole-based pigments, organic pigments such as those based on phthalocyanine, quinacridone, isoindolinone, perylene-perinone, dioxazine, anthraquinone, dianthraquinolyl, 20 anthrapyrimidine, anthanthrone, indanthrone, flavanthrone and pyranthone, pigments based on construction dyestuffs and pigments based on basic dyes, and inorganic pigments such as carbon black, titanium oxide, chrome yellow, cadmium yellow, cadmium red, 25 "benpei", iron black, zinc white, Prussian blue and navy blue.

Pigment dispersant obtained by the present invention is preferably admixed at from 0.1 to 30 parts by weight per 100 parts by weight of pigment. If less 30 than 0.1 part by weight is used, the advantages of pigment dispersant of the present invention are not achieved, and if more than 30 parts by weight are used, the advantages achieved are not proportional with the amount used.

35 The following methods are typical methods for using pigment dispersant of the present invention.

1. Taking pigment composition obtained by mixing pigment and pigment dispersant beforehand, adding said pigment composition to a non-aqueous vehicle or the like, and dispersing.
- 5 2. Adding pigment and pigment dispersant separately to a non-aqueous vehicle or the like, and dispersing.
3. Taking a dispersion obtained by dispersing pigment and pigment dispersant separately beforehand and mixing this dispersion with a non-aqueous vehicle or the like.
- 10 In such cases, the pigment dispersion may be dispersed in solvent alone.
4. Dispersing pigment in a non-aqueous vehicle or the like, then adding pigment dispersant to the resulting dispersion.

15

The desired advantages are achieved with any of these methods.

- Simply mixing powdered pigment dispersant of the present invention with powdered pigment gives
- 20 adequate results as a method for preparing pigment composition as described in 1 above, although better results are achieved by rigorous mixing methods such as mechanical mixing using a kneader, roller, attritor, supermill, various pulverizing machines and the like,
- 25 or adding a solution containing pigment dispersant of the present invention to a suspension of pigment in water or organic solvent and depositing the pigment dispersant onto the pigment surface, or dissolving both organic pigment and pigment dispersant in a strongly
- 30 solubilizing solvent such as sulfuric acid, then coprecipitating using a poor solvent such as water.

- When pigment and pigment dispersant are used as described in 2 to 4 above, better pigment dispersion can be achieved in the pigment in solvent or non-
- 35 aqueous vehicle system, or in the dispersion of pigment dispersant, or in mixtures thereof, by using a dispersing machine such as a dissolver, high-speed mixer, homogenizer, kneader, roll mill, sand mill or attritor.

Thus according to the present invention, in lime rosin varnish, polyamide resin varnish, vinylchloride resin varnish and other such gravure inks, nitrocellulose lacquer, normally dried or baked
5 coatings of aminoalkyd resins, acrylic lacquers, baked aminoacrylic resin coatings, urethane-based resin coatings and other non-aqueous vehicles, fluidity is better than when pigment alone is used (for example, the dispersion viscosity is lower and the structural
10 viscosity is lower) and, at the same time, there are no problems such as color separation or crystal deformation, and the luster of the resulting printed material or coating film is good, and so beautiful products can be obtained.

15 Specifically, pigment dispersants of the present invention yield excellent dispersions not only with oil-modified aminoalkyd resin coatings but also with oil-free alkyd resin coatings.

Moreover, uses of pigment dispersants of the
20 present invention are not limited only to non-aqueous vehicles, as excellent dispersion results and color products of good color strength can be obtained in other printing inks and coatings, and even in the coloration of plastics.

25 A production example for dispersion pigment of the present invention is described below. It should be noted that "parts" below denotes "parts by weight", and the numbers of the pigment dispersants in the production examples are the same as the pigment
30 dispersant numbers given in Table 1.

[Production Example 1]

Compound represented by formula (IV) was
35 chlorosulfonated by a common method, and 50 parts of the resulting compound were dispersed in 900 parts of water. Next, 167 parts of N,N-diethylaminopropylamine were added, and the system was heated to 60°C, then agitated for 2 h at the same temperature. The

precipitate was filtered, then washed with water and dried at 70°C to yield 60 parts of pigment dispersant (1).

5 [Production Example 2]

Compound represented by formula (IV) was converted to di(chloroacetoamidomethyl) by a common method, then 50 parts of the resulting compound were dispersed in
10 900 parts of water. Next, 77 parts of N-aminopropyl-2-pipecoline were added, then the system was heated to 90°C, then agitated for 4 h at the same temperature. The precipitate was filtered, then washed with water and dried at 70°C to yield 68 parts of pigment
15 dispersant (5).

[Production Example 3]

Compound represented by formula (IV) was
20 chloromethylated by a common method, then 50 parts of the resulting compound were dispersed in a mixed solvent comprising 700 parts of water and 100 parts of methanol. Next, 47 parts of dibutylamine were added, and the system was heated to 70°C, then agitated for
25 2 h at the same temperature. The precipitate was filtered, then washed with water and dried at 70°C to yield 59 parts of pigment dispersant (8).

[Production Example 4]

30 77 parts of potassium tert-butoxide and 198 parts of compound represented by formula (VI) were added to 330 parts of anhydrous tert-amyl alcohol in a nitrogen atmosphere, and the system was heated to 85°C. Next,
35 50 parts of dimethylsuccinate were added gradually over 2 h, and the system was agitated for a further 1 h at the same temperature. The system was then cooled to 40°C, 200 parts of methanol were added, the system was then agitated for 15 min, after which the precipitate

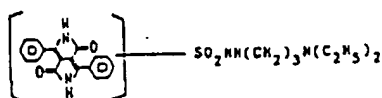
was filtered and washed using water and methanol, then dried at 70°C to yield 147 parts of pigment dispersant (4).

Pigment dispersant of the present invention can be produced by the methods disclosed in Production Examples 1 to 4. Some examples are shown in Table 1.

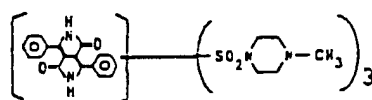
Table 1 Number and structure of pigment dispersant

Number Structure

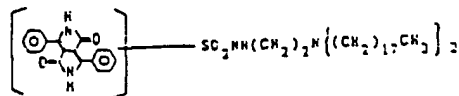
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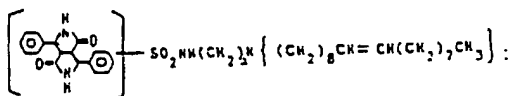
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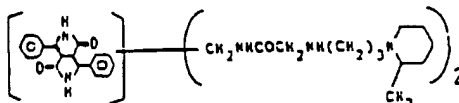
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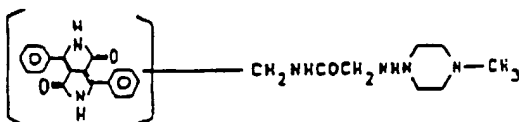
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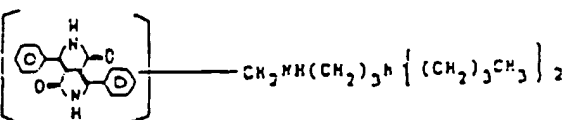
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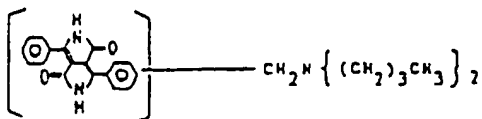


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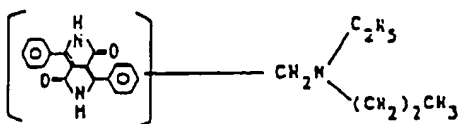


Number Structure

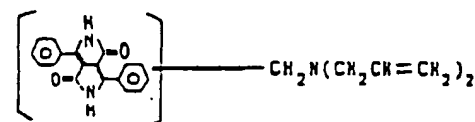
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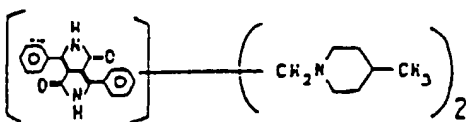
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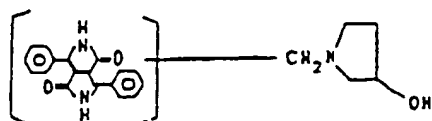
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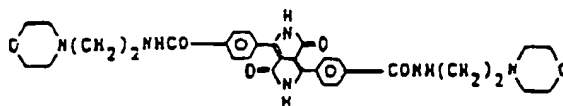
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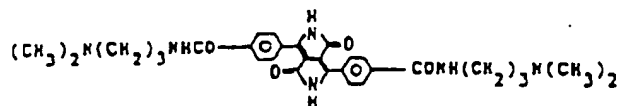
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The following mixed coatings were prepared to appraise pigment dispersants of the present invention.

5	Mixture (1)	
	Pigment	9.5 parts
	Pigment dispersant	0.5 parts
	Alkyd resin varnish	
	(non-volatile component 60%)	26.4 parts
10	Melamine resin varnish	
	(non-volatile component 50%)	13.6 parts
	Thinner (xylene/n-butanol = 8/2)	20 parts
	Mixed varnish added after dispersion	

	(alkyl/melamine = 7/3 (solid component))	48.3 parts
	Mixture (2)	
5	Pigment	9.5 parts
	Pigment dispersant	0.5 parts
	Oil-free polyester resin varnish (non-volatile component 60%)	26.4 parts
	Melamine resin varnish (non-volatile component 50%)	13.6 parts
10	Suwazol	20 parts
	Mixed varnish added after dispersion (alkyl/melamine = 7/3 (solid component))	48.3 parts

15

Coatings were prepared by introducing the abovementioned mixtures into a reaction vessel, adding steel balls and dispersing using a paint shaker. These coatings and coatings obtained without adding pigment dispersant (as the abovementioned mixture, but comprising 10 parts of pigment, with no pigment dispersant added) were compared according to the following appraisal methods. The results are shown in Table 2. It should be noted that the pigment dispersant numbers in Table 2 are the same as the numbers shown in Table 1.

Appraisal method (1)

The viscosity of the coating was judged after being measured using a B-type viscometer (measurement temperature 25°C). It should be noted that the appraisal was a relative comparison with coating with no pigment dispersant added, and the lower the viscosity the better the product.

- O : good
- Δ : quite good
- X : poor

Appraisal method (2)

5 The resulting coatings were adjusted using thinner until they had a final coating viscosity of 23 s using a Ford cup 4, sprayed onto tinplate using an air spray gun, then baked. The 20° gloss was measured by eye and using a glossmeter, and the overall reflective sharpness of the coating surface was appraised.

10

○ : excellent

Δ : good

× : poor

Table 2 Appraisal results

Pigment	Pigment	Mixture (1)		Mixture (2)	
		Appraisal (1)	Appraisal (2)	Appraisal (1)	Appraisal (2)
	B dispersant				
Irgazin DPP red 70	-	x	x	x	x
Irgazin DPP red 70	1	O	O	O	O
Irgazin DPP red 70	4	O	O	O	O
Irgazin DPP red 70	5	O	O	O	O
Irgazin DPP red 70	7	O	O	O	O
Irgazin DPP red 70	13	Δ	O	O	O
C.I. Pig. Blue 15	-	x	x	x	x
C.I. Pig. Blue 15	2	Δ	O	O	O
C.I. Pig. Blue 15	10	O	O	Δ	Δ
C.I. Pig. Red 177	-	x	x	x	x
C.I. Pig. Red 177	11	O	O	Δ	O
C.I. Pig. Red 177	12	O	Δ	O	O
C.I. Pig. Red 168	-	x	x	x	x
C.I. Pig. Red 168	6	O	O	Δ	O
C.I. Pig. Red 168	9	Δ	O	O	O
C.I. Pig. Yellow 108	-	x	x	x	x
C.I. Pig. Yellow 108	6	Δ	Δ	O	O
C.I. Pig. Yellow 108	9	O	O	O	O
C.I. Pig. Violet 19	-	x	x	x	x
C.I. Pig. Violet 19	3	O	O	O	O
C.I. Pig. Violet 19	9	O	O	O	O
C.I. Pig. Violet 23	-	x	x	x	x
C.I. Pig. Violet 23	1	Δ	O	Δ	O
C.I. Pig. Violet 23	7	O	O	Δ	O
C.I. Pig. Blue 60	-	x	x	x	x
C.I. Pig. Blue 60	5	O	O	Δ	O
C.I. Pig. Blue 60	10	O	O	Δ	Δ
C.I. Pig. Yellow 24	-	x	x	x	x
C.I. Pig. Yellow 24	4	O	O	Δ	O
C.I. Pig. Yellow 24	12	O	Δ	O	O
C.I. Pig. Orange 43	-	x	x	x	x
C.I. Pig. Orange 43	8	Δ	O	O	O
C.I. Pig. Orange 43	13	O	O	O	O
C.I. Pig. Red 178	-	x	x	x	x
C.I. Pig. Red 178	2	O	O	O	Δ
C.I. Pig. Red 178	11	O	O	Δ	Δ
C.I. Pig. Red 179	-	x	x	x	x
C.I. Pig. Red 179	1	O	O	O	O
C.I. Pig. Red 179	14	O	O	Δ	O
C.I. Pig. Red 149	-	x	x	x	x
C.I. Pig. Red 149	3	Δ	Δ	O	O
C.I. Pig. Red 149	10	O	O	Δ	O
C.I. Pig. Red 123	-	x	x	x	x
C.I. Pig. Red 123	2	Δ	O	O	O
C.I. Pig. Red 123	9	O	O	O	Δ
C.I. Pig. Red 190	-	x	x	x	x
C.I. Pig. Red 190	6	O	Δ	O	Δ
C.I. Pig. Red 190	7	O	O	Δ	O
C.I. Pig. Yellow 12	-	x	x	x	x
C.I. Pig. Yellow 12	1	O	O	O	O
C.I. Pig. Yellow 12	8	O	O	Δ	Δ
C.I. Pig. Red 176	-	x	x	x	x
C.I. Pig. Red 176	11	Δ	O	Δ	O
C.I. Pig. Red 176	13	O	O	Δ	Δ
C.I. Pig. Black 6	-	x	x	x	x
C.I. Pig. Black 6	1	O	O	Δ	O
C.I. Pig. Black 6	14	Δ	O	Δ	O

These coatings were left to stand for 1 week, then their viscosity was measured using the same viscometer, and there was almost no increase in viscosity. Also, a pale coating (cut 1/10 using white coating adjusted using titanium white) was prepared, its viscosity was adjusted to 23 s using a Ford cup 4, and a sample was taken in a test tube and the flocculation was observed by eye, whereupon even after 1 week no color separation or precipitation was seen.

Moreover, pigment with added pigment dispersant of the present invention exhibited good dispersion properties and did not flocculate even in nitro-cellulose lacquer, acrylic resin coatings and gravure inks.

Patent Applicant

Toyo Ink Seizo K.K.

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